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# **Photon funnels for one-way energy transfer: multimetallic assemblies incorporating cyclometallated iridium or rhodium units accessed by sequential cross-coupling and bromination**

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## **Abstract**

The generation of multimetallic assemblies is a widely explored theme, owing to the relevance of controlling energy- and electron-transfer between metal centres to many fields of contemporary importance. Boronic acid-substituted coordination and organometallic complexes have been shown to be useful synthons in the formation of such structures through cross-coupling with halogenated complexes. Here we use such methodology to generate an octanuclear mixed-metal compound of composition  $\text{Ir}_7\text{Ru}$ , having a dendrimer wedge-like structure. The method combines cross-coupling with regiospecific bromination of phenylpyridine (ppy) ligands at the position *para* to the C–Ir bond. The propensity of  $\text{Ir}(\text{ppy})_2$ -based complexes to electrophilic bromination is found to be deactivated by the introduction of fluorine atoms. The coupling methodology is extended to rhodium-containing systems, exemplified by a tetranuclear system of composition  $\text{Rh}_2\text{Ir}_1\text{Ru}_1$ . The synthesis requires the use of boronic acid-appended  $\text{Rh}(\text{III})$  complexes, which can be accessed by introduction of a neopentyl-boronate ester-appended bipyridine into the coordination sphere of  $\text{Rh}(\text{III})$ . In the resulting multinuclear complexes, the excited state energies of the constituent metal units are such that unidirectional energy transfer occurs from the  $\text{Rh}(\text{III})$  /  $\text{Ir}(\text{III})$  branches to the  $\text{Ru}(\text{II})$  core. The luminescence thus resembles that of an isolated  $[\text{Ru}(\text{bpy})_3]^{2+}$  unit but the ability of the structure to collect light is greatly enhanced.

## Introduction

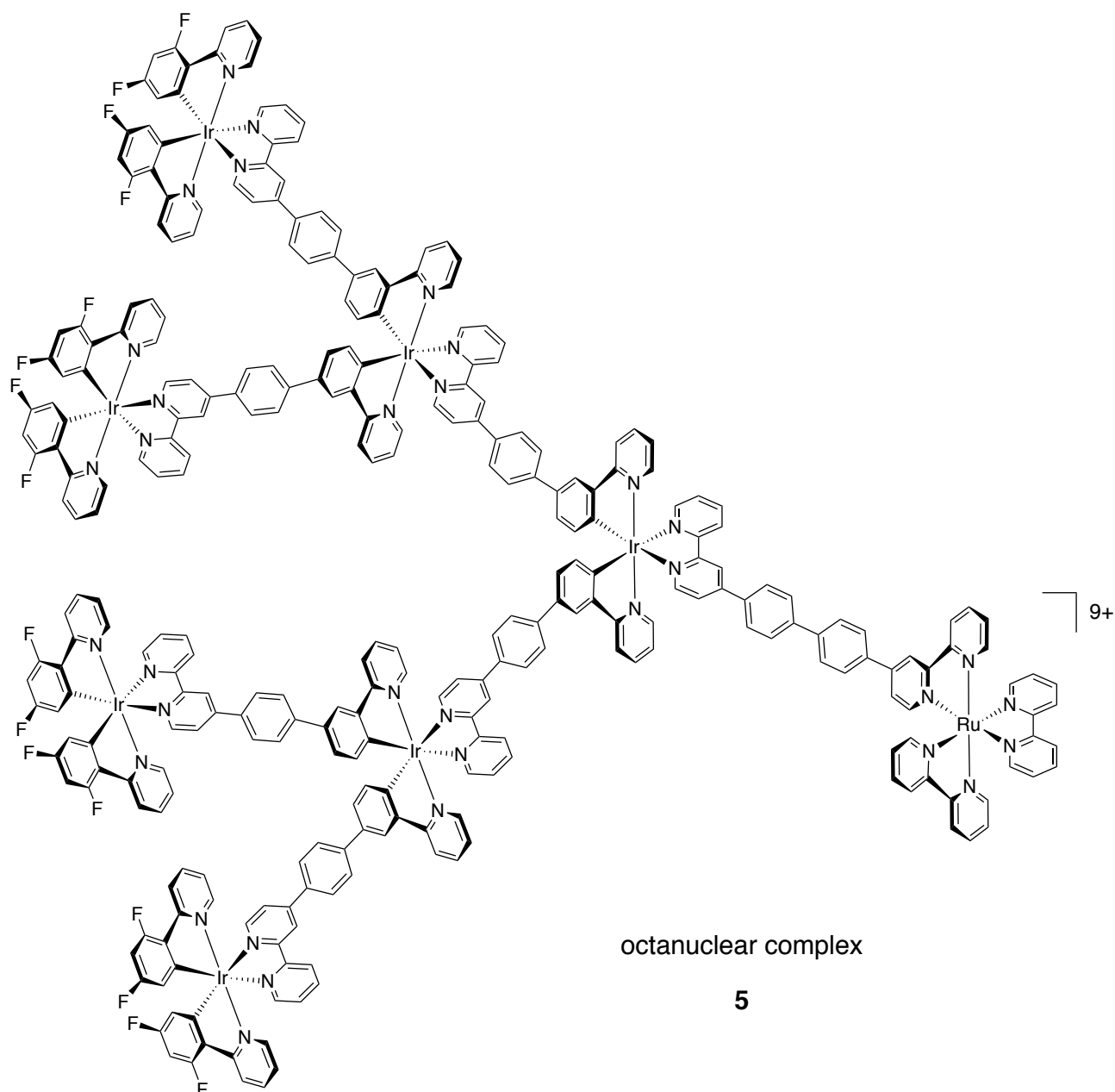
The generation of multimetallic assemblies incorporating linked metal complex units has been central to the area of supramolecular chemistry since its inception.<sup>[1]</sup> Highly sophisticated structures have been generated, in some cases by self-assembly using the metal as a template and in others by forming covalent bonds between existing units. The field of supramolecular *photochemistry* has been dominated by metal complexes, particularly those based on 2<sup>nd</sup> and 3<sup>rd</sup>-row d<sup>6</sup> metal ions such as Ru(II), Os(II), Ir(III) and Re(I).<sup>[2,3]</sup> A key theme has been the quest to control energy- and electron-transfer processes between metal centres – processes that are particularly relevant to solar energy conversion, but also of interest in electroluminescence, nonlinear optics and optical information storage for example.<sup>[4,5,6]</sup> Whilst early work favoured ruthenium(II) diimine systems, more recent studies have turned increasingly to bis- and tris-cyclometallated iridium(III) chemistry, owing to the higher quantum yields and greater scope for tuning of excited-state energies.<sup>[7,8]</sup>

In terms of their photophysics, multinuclear iridium structures tend to fall at one of two ends of a spectrum. The photophysical properties of the assembly may be fundamentally different from those of related mononuclear complexes: there may be very large effects on the singlet and triplet excited state energies. For example, we have shown how 4,6-diphenylpyrimidine can act as a bis-*N*<sup>^</sup>C-bridging ligand to form multinuclear complexes that are characterised by much lower absorption and emission energies than their mononuclear counterparts.<sup>[9]</sup> At the other extreme, the individual units may retain, to a significant extent, properties that are similar to those of the isolated units, with the bridging unit playing a relatively minor role other than that of bringing the units into close proximity. In such cases, the absorption profile of the assembly may be quite similar to the summation of the individual components.<sup>10</sup> Examples include several compounds that make use of *para*-phenylene-bridged bis-bipyridines to link two Ir(ppy)<sub>2</sub> units.<sup>[11]</sup> Typical synthetic approaches to such heterometallic assemblies involve prior synthesis

of multitopic ligands, but such an approach requires subsequent stepwise and selective metal complexation, which can be difficult to control. The alternative strategy of “chemistry on the complex” has emerged as an attractive alternative, where pre-formed complexes are linked together, for example, through C–C bond-forming reactions.<sup>[12,13]</sup>

We previously developed the synthesis of boronic acid-substituted ruthenium(II) and iridium(III) complexes, and demonstrated that they can readily undergo Suzuki-type cross-coupling reactions with halogenated complexes.<sup>[14,15,16,17]</sup> For complexes with cyclometallating ligands, such as those based on Ir(ppy)<sub>2</sub> units, the strategy can become yet more powerful, since it may be possible to introduce halogen functionality into the multimetallic products under mild conditions.<sup>[15,17]</sup> The propensity of aryl rings to electrophilic bromination is increased upon metallation with platinum group metals such as iridium(III) or ruthenium(II), specifically at the position *para* to the C–M bond.<sup>[18,19]</sup> Previously, we made use of this reactivity to prepare di-, tri- and tetranuclear complexes.<sup>[15a,17]</sup>

In this work, we describe how repetitive use of this methodology – sequences of cross-coupling and *in situ* bromination – can be employed to produce larger structures, in this case, an octameric mixed-metal complex **5** with a dendrimer wedge-like structure (Fig. 1). The excited state energies of the constituent units are such that unidirectional energy-transfer occurs from the branches of the system to the core. We also show that similar chemistry can be applied to rhodium-containing molecular materials, through the synthesis of boronic acid-appended Rh(III) complexes. The synthesis of a trimetallic, tetranuclear compound **9** – containing two bis-cyclometallated rhodium(III) centres, one central iridium(III) unit and one terminal tris-bipyridyl ruthenium(II) moiety – is described.



**Figure 1** The structure of the multimetallic ( $\text{Ir}_7\text{Ru}_1$ ) octanuclear complex **5** reported in this work

## Results and discussion

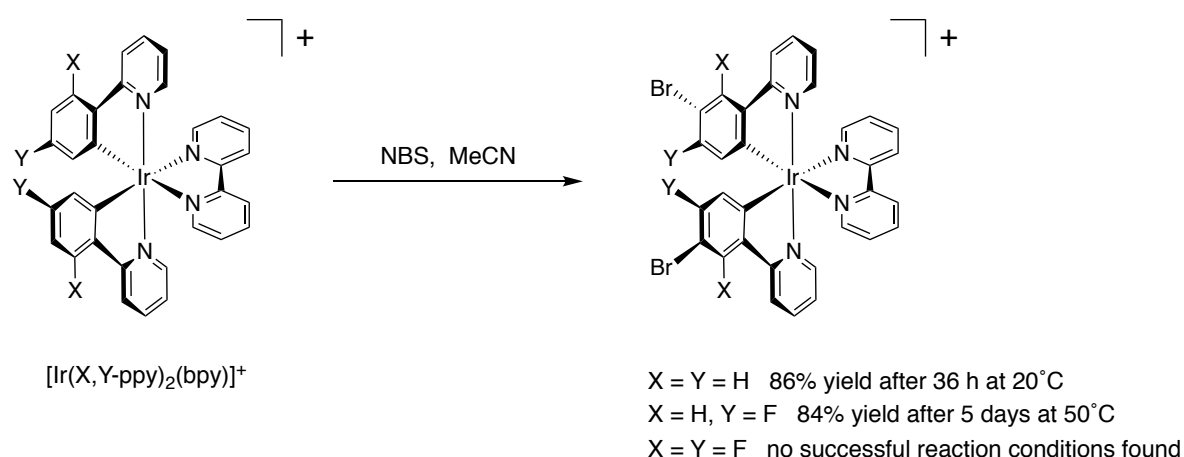
### *Synthetic strategies*

As constituent “building blocks” for our work, we chose to employ the combination of tris-bipyridyl ruthenium complexes based on  $[\text{Ru}(\text{bpy})_3]^{2+}$  and the well-known class of bis-cyclometallated iridium(III) complexes of which  $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$  is the archetypal example.<sup>[20]</sup>

This choice was driven by the rich photochemical and photophysical properties of such compounds, particularly their luminescence properties and well-established control over excited

state energies.<sup>[21,22]</sup> The synthetic strategy is summarised in Scheme 2. Key to the stepwise synthesis is the fact that  $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$  can be brominated under very mild conditions, regiospecifically at the carbon *para* to the C–Ir bond (Scheme 1).<sup>[15a]</sup> The reaction proceeds smoothly using N-bromosuccinimide (NBS) as the brominating agent in acetonitrile solution at room temperature.

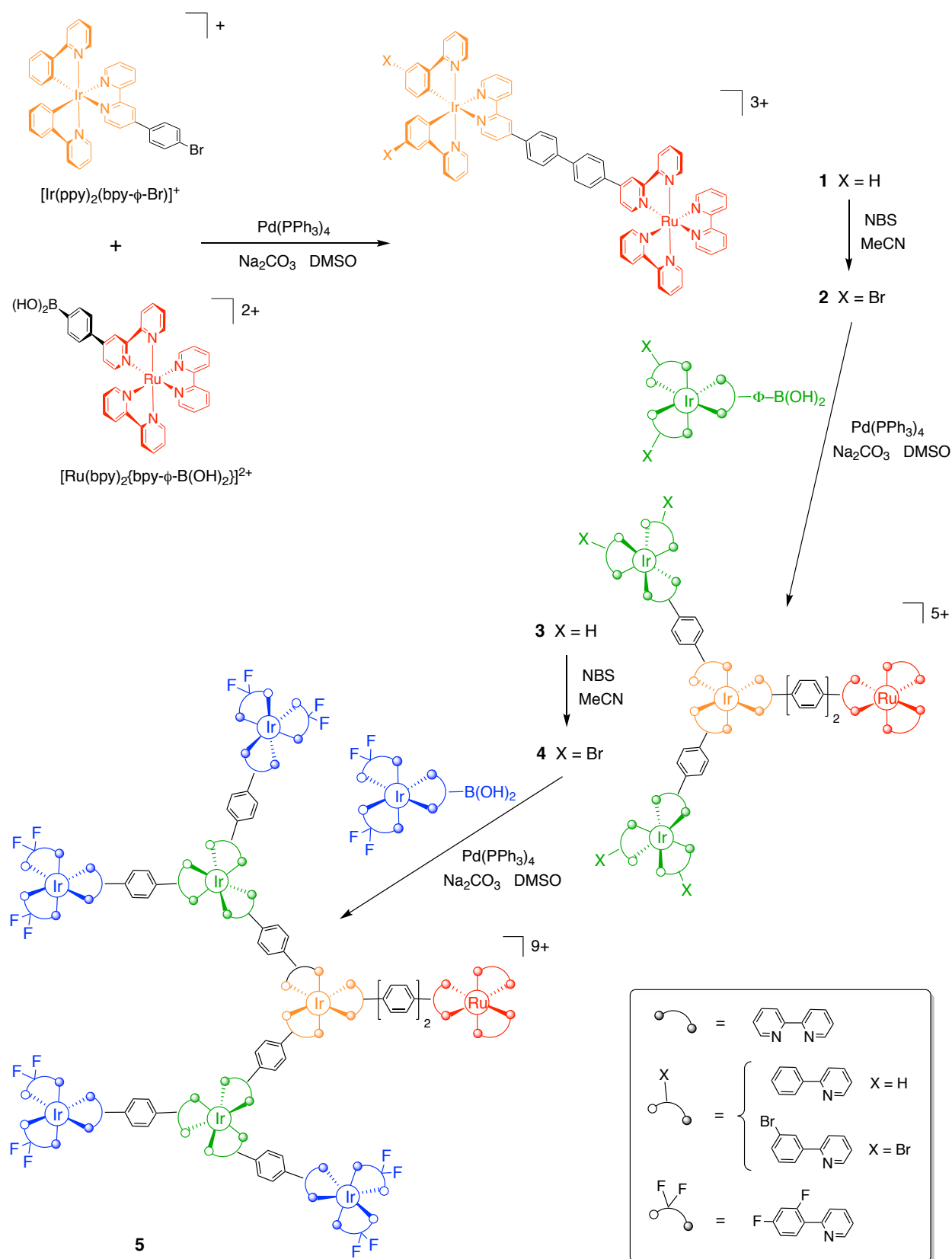
As part of this work, we sought to extend this chemistry to analogues with 2-(4-fluorophenyl)-pyridine (Fppy) ligands. No reaction of  $[\text{Ir}(\text{Fppy})_2(\text{bpy})]^+$  with NBS was observed at room temperature, even after one week. However, by using an excess of NBS and increasing the temperature to 50°C, bromination could be induced (Scheme 1). Importantly, the reaction remains regiospecific: the site of bromination is exclusively the position *para* to the C–Ir bond. On the other hand, in the case of complexes of 2-(2,4-difluoro-phenyl)pyridine (F<sub>2</sub>ppy) – incorporating *two* fluorine atoms in each phenyl ring and flanking the *para* C–H bond – no reaction was observed even when employing a large excess of NBS and prolonged elevated temperatures. The decrease in reactivity associated with the introduction of fluorine atoms is presumably due to the combined electronic and steric effects associated with the F atoms.



**Scheme 1** Bromination of bis-cyclometallated iridium(III) complexes and the detrimental effect of flanking fluorine atoms.

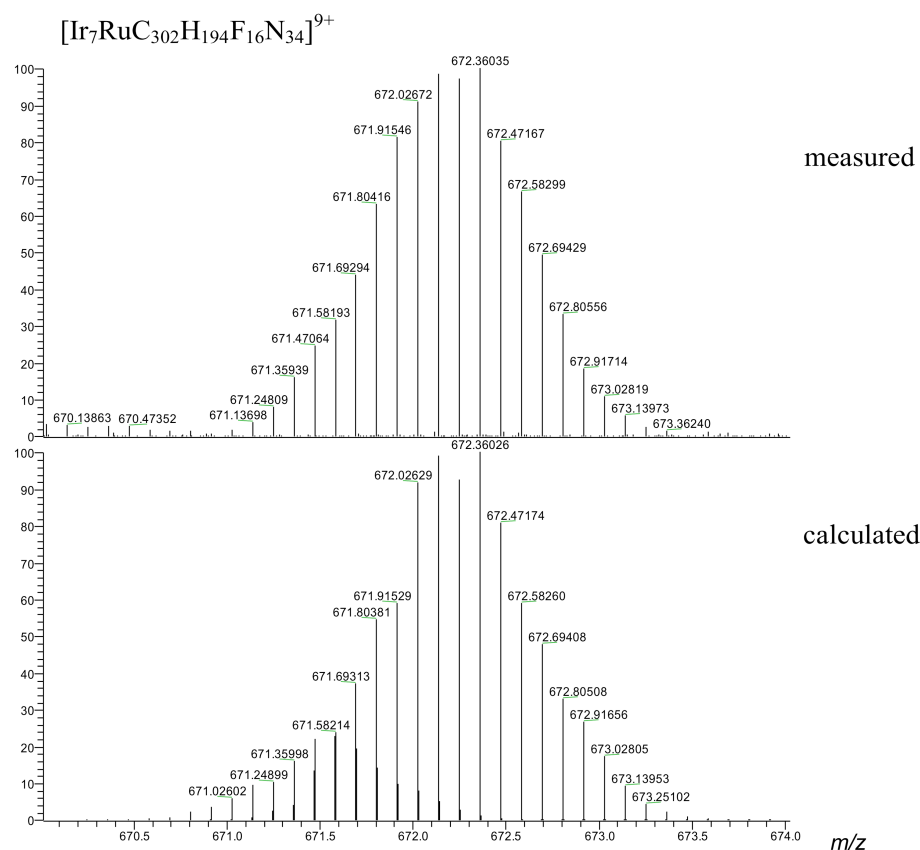
The tetranuclear complex **3** was synthesised using a procedure similar to that described previously by us for a related complex incorporating F<sub>2</sub>ppy ligands on the peripheral iridium centres.<sup>[12]</sup> First, an iridium complex incorporating a bromophenyl pendent [Ir(ppy)<sub>2</sub>(bpy-φ-Br)]PF<sub>6</sub> was cross-coupled with a ruthenium complex containing a pendent boronic acid [Ru(bpy)<sub>2</sub>{bpy-φ-B(OH)<sub>2</sub>}(PF<sub>6</sub>)<sub>2</sub>] (Scheme 2). The resulting dinuclear complex [Ir(ppy)<sub>2</sub>(bpy-φ-φ-bpy)Ru(bpy)<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub> **1** was then treated with NBS as described above, leading to the dibrominated complex incorporating one Br atom in each of the two ppy ligands, [Ir(Br-ppy)<sub>2</sub>(bpy-φ-φ-bpy)Ru(bpy)<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub>, **2**. Subsequent cross-coupling with [Ir(ppy)<sub>2</sub>{bpy-φ-B(OH)<sub>2</sub>}]PF<sub>6</sub> led to tetranuclear complex **3**(PF<sub>6</sub>)<sub>5</sub>. Treatment with NBS gave the tetrabrominated complex **4**(PF<sub>6</sub>)<sub>5</sub>, from which octanuclear complex **5**(PF<sub>6</sub>)<sub>9</sub> was obtained following cross-coupling with 4 equivalents of [Ir(F<sub>2</sub>ppy)<sub>2</sub>{bpy-φ-B(OH)<sub>2</sub>}]PF<sub>6</sub> (Scheme 3). The identity and purity of the product were confirmed with the aid of electrospray mass spectrometry, where isotope matching of the highly charged ions proved to be particularly informative (Figure 2).

The parent complexes [Ru(bpy)<sub>3</sub>]<sup>+</sup> and [Ir(ppy)<sub>2</sub>(bpy)]<sup>+</sup> display one-electron oxidation and reduction processes at relatively accessible potentials; E<sup>ox</sup> = +1.26 and +1.24 V respectively and E<sup>red</sup> = -1.28 and -1.41 V, respectively, in acetonitrile versus SCE.<sup>4,7</sup> For both classes of complex, the site of reduction is the bipyridine, whilst the oxidation is metal-based Ru(II)→Ru(III) or Ir(III)→Ir(IV) (although in the latter case, the high degree of covalency of the C–Ir bonds means that such a description is an approximation). Using square wave voltammetry in acetonitrile solution, octanuclear complex **5** was found to display a single oxidation process at 1.33 V whilst the first reduction process is a strong band at -1.20 V (Figure S1 in the Supporting Information). These values are similar to those of the simple, unsubstituted mononuclear complexes. Individual processes associated with each metal unit are apparently not resolved, at least under the conditions employed at ambient temperature. One may tentatively infer that there is little ground-state communication between the metal units.



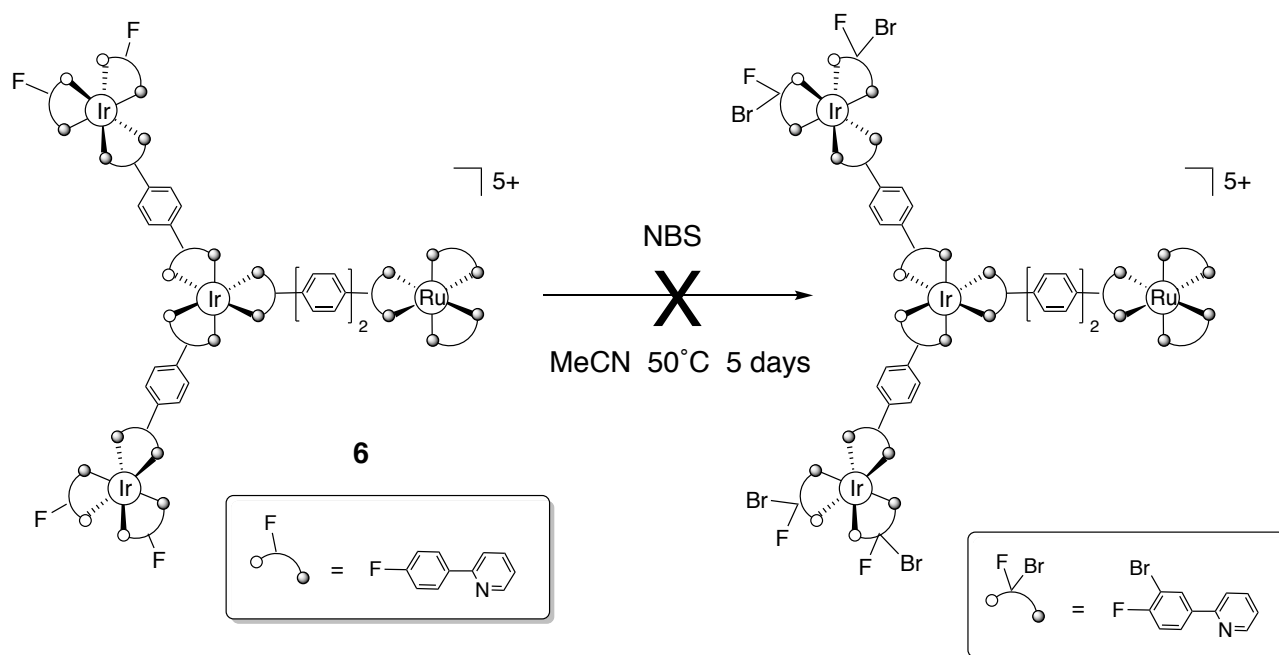
**Scheme 2** Synthetic route to **5** via sequential cross-coupling and in situ bromination. For clarity, bidentate ligands are shown as hemispheres in **3–5**; the full structure of **5** is given in Figure 1.





**Figure 2** Measured (top) and calculated (bottom) mass spectra for the 9+ cation of complex 5 recorded using electrospray ionisation.

We also prepared the analogue of **3** that incorporates mono-fluorinated Fppy ligands at the periphery, namely tetranuclear complex **6** (Scheme 3). This compound was prepared in the same way as **3** but by using  $[\text{Ir}(\text{Fppy})_2\{\text{bpy}-\phi-\text{B}(\text{OH})_2\}]\text{PF}_6$  in place of  $[\text{Ir}(\text{ppy})_2\{\text{bpy}-\phi-\text{B}(\text{OH})_2\}]\text{PF}_6$  in the final step. However, despite the success of bromination of the mononuclear Fppy-containing complex  $[\text{Ir}(\text{Fppy})_2(\text{bpy})]^+$  (Scheme 1), the reaction did not proceed cleanly when applied to **6**. Analysis of the reaction mixture by electrospray mass spectrometry revealed the presence of a mixture of several bromination products, including a species containing five bromine atoms, whereas the desired product contains only four. Not surprisingly, it was not possible to separate the different bromination products chromatographically, all apparently having essentially the same  $R_f$  value.

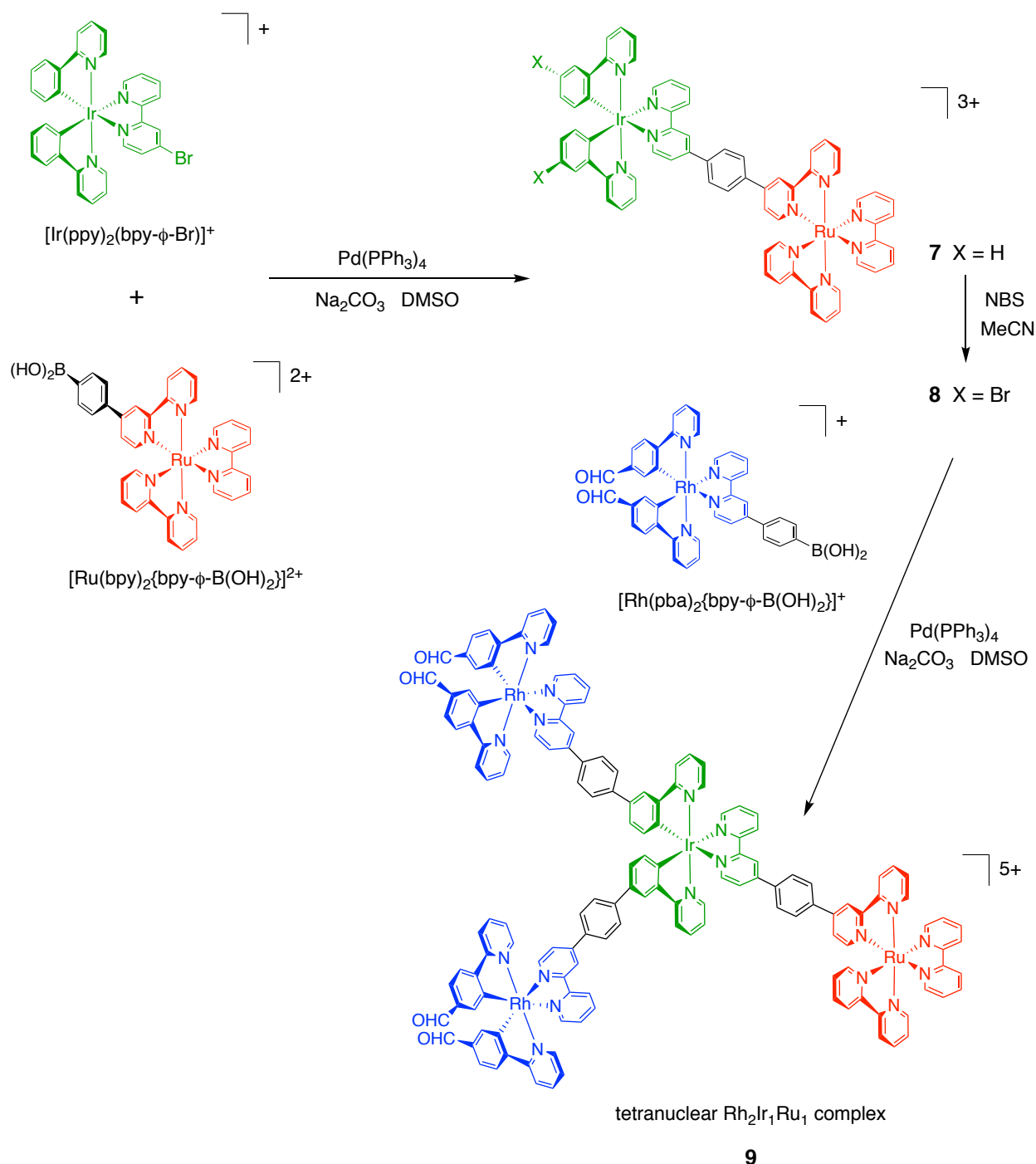


**Scheme 3** Attempted bromination of **6**, under conditions used successfully for mononuclear  $[\text{Ir}(\text{Fppy})_2(\text{bpy})]^+$  (Scheme 1) does not lead cleanly to the desired tetrabrominated complex but to a mixture of products as detected by ESI-MS.

#### **Tetranuclear system comprising three metals Rh, Ir and Ru**

To explore the possibility of incorporation of rhodium units into multinuclear assemblies, using the cross-coupling methodology, we chose to target the tetranuclear system **9**, containing Rh(III), Ir(III) and Ru(II) (Scheme 4). Compound **9** would constitute a particularly challenging target for synthesis using pre-formed bridging ligands, owing to the presence of the different metals having similar reactivity with diimine ligands. Rhodium(III) complexes of  $N^{\wedge}C$ -cyclometallating ligands have been much less investigated than their iridium(III) analogues, partly because of the generally lower emission efficiencies associated with the smaller spin-orbit coupling constant of the 2<sup>nd</sup> row element, and probably also because of the higher cost of rhodium.<sup>[23]</sup> The choice of Rh units here, namely those based on  $\text{Rh}(N^{\wedge}C\text{-pba})_2$  units (where pba = 4-pyridylbenzaldehyde), was inspired by the work of Lo and co-workers, who noted that the introduction of aldehyde functionality led to higher-energy, longer-lived and more intense emission in  $[\text{Rh}(\text{pba})_2(N^{\wedge}N)]^+$  complexes as compared to analogues with unsubstituted ppy ligands.<sup>[24]</sup> They observed triplet emission energies of around  $20000 \text{ cm}^{-1}$  for these complexes. Being significantly higher than

that of  $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ , for which the value is around  $16500\text{ cm}^{-1}$ , this should make the  $[\text{Rh}(\text{pba})_2(\text{N}^{\wedge}\text{N})]^+$  class of complex attractive as energy donors in the sorts of assemblies for directional transfer energy transfer which our work seeks to develop.

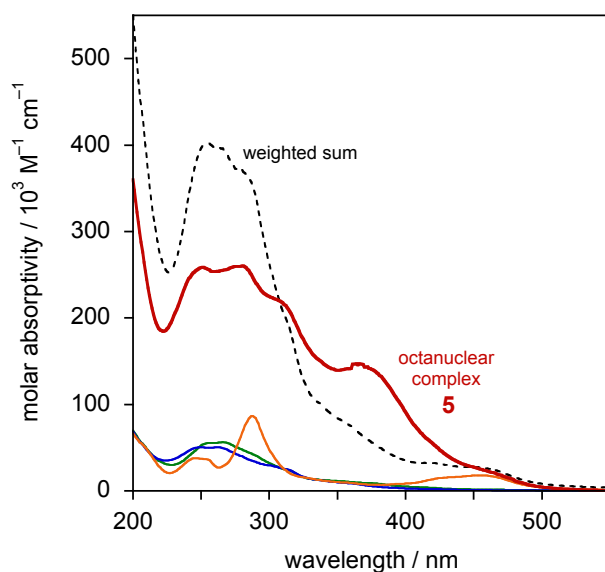


**Scheme 4** Synthetic route to the tetranuclear, trimetallic  $\text{Rh}_2\text{Ir}_1\text{Ru}_1$  complex **9** via sequential cross-coupling and in situ bromination.

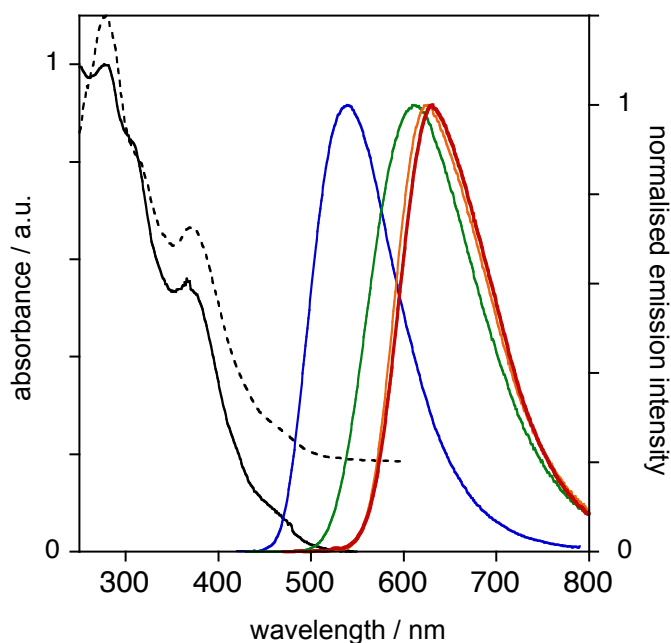
The synthesis of **9** involved a similar strategy to that of **3** and **6** and is summarised in Scheme 4. It requires the use of boronate-substituted rhodium complexes, for which we are aware of no precedent in the literature. It was found that the strategy previously developed for boronic acid-appended iridium(III) and ruthenium(II) complexes<sup>[14,15]</sup> could be applied equally well to rhodium. Thus, the requisite complex  $[\text{Rh}(\text{N}^{\wedge}\text{C-pba})_2\{\text{N}^{\wedge}\text{N-bpy-}\phi\text{-B(OH)}_2\}]\text{PF}_6$  could be obtained by treatment of  $[\text{Rh}(\text{pba})_2(\mu\text{-Cl})]_2$  with the 4-neopentylboronate ester of 4-phenylbipyridine in a mixture of  $\text{CH}_2\text{Cl}_2$  and MeOH. After 90 min at reflux, aqueous work-up and precipitation from  $\text{KPF}_6(\text{aq})$  led to the desired complex in sufficient purity for use directly in the subsequent cross-coupling reaction. Thus, dinuclear complex **7** (which resembles **1** but with just one phenyl ring between the two metal units) was prepared by an initial Pd-catalysed cross-coupling of  $[\text{Ir}(\text{ppy})_2(\text{bpy-Br})]^+$  with  $[\text{Ru}(\text{bpy})_2\{\text{bpy-}\phi\text{-B(OH)}_2\}]^+$ , brominated upon treatment with NBS in acetonitrile to give **8**, and finally cross-coupled with the boronate-substituted rhodium(III) complexes to generate the target compound **9**. The crude product was precipitated from  $\text{KPF}_6(\text{aq})$  and purified by column chromatography on silica using a water / acetonitrile gradient.

### ***Photophysical properties of multimetallic complexes***

The photophysical properties of the octanuclear complex **5** were investigated in acetonitrile solution (Table 1 and Figures 3 and 4). The absorption spectrum is of similar shape to the sum of the spectra of the constituent monometallic building block complexes, but with increased absorption between 330 and 410 nm, and decreased absorption between 240 and 300 nm (Figure 3). This is likely to be due to the increased conjugation in the octanuclear species in comparison to the building blocks, shifting some of the ligand-centred transitions to lower energy. Similar observations have been made for other multinuclear complexes with polyphenylene bridges.<sup>[11,15,16]</sup>



**Figure 3** Absorption spectra of octanuclear ( $\text{Ir}_7\text{Ru}$ ) complex **5** (thick red solid line) and of the constituent “building-block” complexes:  $[\text{Ru}(\text{bpy})_2(\text{bpy-Ph})]^{2+}$  (orange),  $[\text{Ir}(\text{ppy})_2(\text{bpy-Ph})]^+$  (green) and  $[\text{Ir}(\text{F}_2\text{ppy})_2(\text{bpy-Ph})]^+$  (blue), as their  $\text{PF}_6$  salts in acetonitrile at  $298 \pm 3 \text{ K}$  in each case. The weighted sum of the component mononuclear complexes (i.e. in ratio 1:1:2) is given by the black dashed line.



**Figure 4** Left: absorption spectrum (black solid line) and excitation spectrum ( $\lambda_{\text{em}} = 630 \text{ nm}$ , dashed line) of octanuclear complex **5** in acetonitrile at  $298 \pm 3 \text{ K}$ . Right: emission spectrum of **5** under the same conditions (thick red line), together with the emission spectra of the constituent “building-block” complexes represented as indicated in the caption to Fig. 3.

**Table 1** Photophysical properties of the octanuclear  $Ir_7Ru_1$  compound **5** and tetranuclear  $Rh_2Ir_1Ru_1$  **9** together with relevant model mononuclear complexes of Ru(II), Ir(III) and Rh(III) for comparison

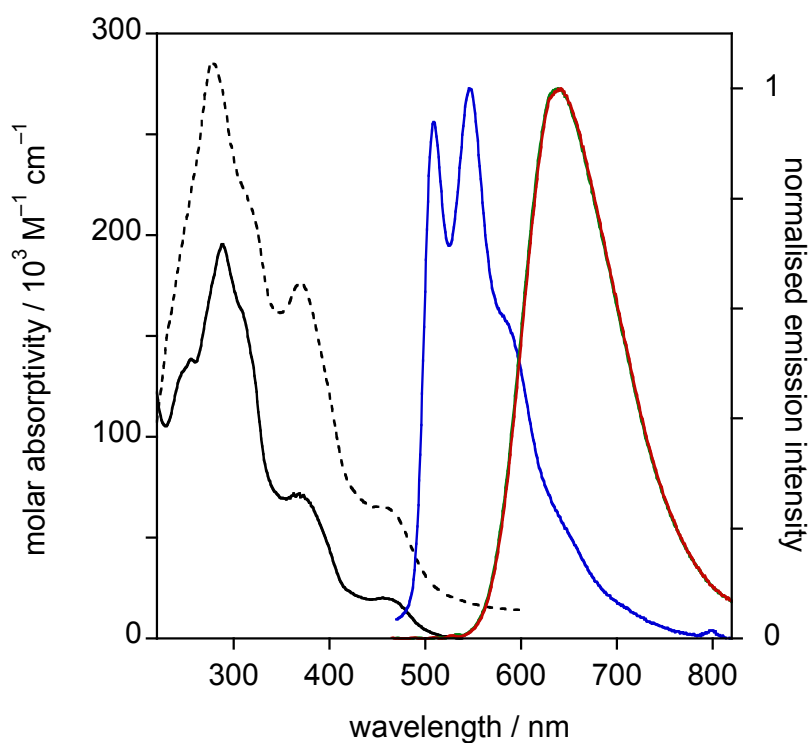
Compound <sup>(a)</sup>	Absorption <sup>(b)</sup> $\lambda_{\max} / \text{nm} (\epsilon / 10^3 \text{ M}^{-1}\text{cm}^{-1})$	Emission $\lambda_{\max} / \text{nm}$	$\Phi \times 10^2$ <sup>(c)</sup>	Lifetime / ns <sup>(d)</sup>
<b>5</b> <sup>9+</sup> ( $Ir_7Ru_1$ )	252 (260), 280 (262), 303 (224), 368 (148), 455 (25.2)	630	12	1600 [210]
$[\text{Ir}(\text{ppy})_2(\text{bpy-Ph})]^+$	256 (54.1), 267 (54.8), 312 (23.6), 337 (12.0), 374 (8.15), 404 (4.04), 466 (0.997)	613	13	410 [80]
$[\text{Ir}(\text{F}_2\text{ppy})_2(\text{bpy-Ph})]^+$	250 (49.2), 262 (49.1), 300 (28.1), 313 (23.5), 333 (12.1), 359 (7.86), 417 (1.3), 446 (598)	539	66	1400 [140]
$[\text{Ru}(\text{bpy})_2(\text{bpy-Ph})]^+$	246 (36.3), 263 (35.0), 288 (84.1), 399 (7.03), 430 (14.0), 454 (16.9)	627	9.0	1300 [200]
$[\text{Rh}(\text{pba})_2(\text{bpy-Ph})]^+$	254 (34.6), 272 (41.6), 295 (34.0), 310 (32.1), 317 (27.3), 393 (4.81)	508, 546, 584sh	0.90	7900 [620]
<b>9</b> <sup>5+</sup> ( $Rh_2Ir_1Ru_1$ )	256 (128), 289 (175), 309 (146), 369 (67.0), 456 (20.2)	640	15	2000 [260]

(a) As  $\text{PF}_6^-$  salts in each case, in solution in MeCN at  $298 \pm 3\text{K}$ . (b) Bands  $> 250 \text{ nm}$  are listed. (c) Luminescence quantum yield in deoxygenated solution, measured using  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2(\text{aq})$  as the standard. (d) In deoxygenated solution; values in parenthesis are for air-equilibrated solution.

Upon photo-excitation in solution, a single emission band is observed at 630 nm, irrespective of the excitation wavelength selected. The emission is characterised by a lifetime of 1.6  $\mu\text{s}$  in deoxygenated MeCN at room temperature and the luminescence quantum yield was measured to be 0.12 under these conditions. These luminescence parameters are characteristic of emission from the tris-bipyridyl ruthenium(II) moiety.<sup>[25]</sup> The close match between the excitation spectrum registered at 630 nm and the absorption spectrum (Figure 4) confirms that excitation of any part of the molecule is followed by rapid energy transfer to the ruthenium terminus of the dendrimer wedge, from which emission then occurs. The unidirectional energy transfer will be

favoured by the gradation in excited state energies intrinsically built into the system, namely  $[\text{Ir}(\text{F}_2\text{ppy})(\text{bpy-Ph})]^+ > [\text{Ir}(\text{ppy})_2(\text{bpy-Ph})]^+ > [\text{Ru}(\text{bpy})_2(\text{bpy-Ph})]^{2+}$ . The phenylene bridges are seen to facilitate energy transfer whilst at the same time ensuring that the properties of the individual building blocks are largely retained. The lack of detectable emission from the  $[\text{Ir}(\text{F}_2\text{ppy})(\text{bpy-ph})]^+$  units, which would be expected at higher energies as shown by the blue line in Fig. 4, allows the energy transfer rates to be estimated to be at least  $2 \times 10^8 \text{ s}^{-1}$ , using a previously described analysis which assumes that detection of bands down to 5% of the intensity of the main band would be detectable.<sup>[26,27]</sup> Rate constants of energy transfer slower than around this value would lead to residual emission associated with the  $\text{Ir}(\text{F}_2\text{ppy})_2$  units being observed.

Similar observations have been made for the  $\text{Rh}_2\text{Ir}_1\text{Ru}_1$  system **9**, whose absorption and emission properties are summarised in Figure 5 and Table 2. Photo-excitation of this compound leads to a broad emission band centred at 640 nm, similar to  $[\text{Ru}(\text{bpy})_2(\text{bpy-Ph})]^{2+}$  but slightly red-shifted. The spectrum is essentially the same as that of  $[\text{Ir}(\text{ppy})_2(\text{bpy})\text{-}\phi\text{-}\phi\text{-bpyRu}(\text{bpy})]^{3+} **7** (Figure 5). The model mononuclear complex  $[\text{Rh}(\text{pba})_2(\text{bpy-Ph})]^+$ , on the other hand, displays a structured spectrum with  $\lambda_{(0-0)} = 508 \text{ nm}$ . There is no evidence of any residual such emission in the spectrum of **9**, indicative – again – of fast energy transfer, in this case from the Rh periphery of the molecule towards the Ru terminus.$



**Figure 5** Left: absorption spectrum (black solid line) and excitation spectrum ( $\lambda_{em} = 640$  nm, dashed line) of tetranuclear complex **9** in acetonitrile at  $298 \pm 3$  K. Right: emission spectrum of **9** under the same conditions (red line), together with the emission spectra of the model mononuclear complex  $[Rh(pba)_2(bpy-Ph)]^+$  (blue line) and dinuclear  $Ir_1Ru_1$  complex **7** (green line, barely visible under the spectrum of **9**);  $PF_6$  salts in MeCN in each case.

## Concluding remarks

In this contribution, we have shown how cross-coupling reactions followed by *in situ* bromination of the resulting products can be used provide access to multimetallic assemblies under mild and well-controlled conditions. In the generation of the octanuclear complex **5**, three cross-couplings and two brominations are used, in each case generating well-defined products. Notably, despite the high overall positive charge on the multinuclear products (e.g.  $9+$  in the case of **5**), the charge is spread over a large molecular volume such that the products remain amenable to column chromatography under conditions not dissimilar to those used for simple mononuclear derivatives of  $[Ru(bpy)_3]^{2+}$ .



It is found that fluorine atoms in the phenyl ring of ppy ligands lead to a reduction in the rate of the *in situ* bromination of their bis-cyclometallated iridium complexes. Complexes of Fppy remain amenable to the reaction, although they require larger quantities of NBS, longer reaction times and elevated temperatures compared to their Ir(ppy)<sub>2</sub> analogues. When incorporated within a multinuclear assembly, however, the reactivity of the Ir(Fppy)<sub>2</sub> unit seems to be further reduced, and the reaction does not lead cleanly to the single desired product containing only one Br per Fppy. Meanwhile, Ir(F<sub>2</sub>ppy)<sub>2</sub>-based complexes show no propensity at all to electrophilic bromination using NBS as the reagent.

Cross-couplings are shown to be possible also using boronic acid-appended rhodium(III) complexes. Boronic acid functionality can be introduced in a similar manner to the iridium(III) systems, by reaction of [Rh(*N*<sup>^</sup>C)<sub>2</sub>(μ-Cl)]<sub>2</sub> dimers with a bipyridine carrying a neopentyl boronate ester; the ester hydrolyses to the boronic acid during the reaction and/or aqueous work-up of the resulting complex. The utility of such a complex has been exemplified through the preparation of the tetranuclear Rh<sub>2</sub>Ir<sub>1</sub>Ru<sub>1</sub> complex **9**.

In the multinuclear assemblies that are formed using this strategy, the metal units are linked by biphenyl units that offer only a limited degree of conjugation between them, owing to the twisting of adjacent rings relative to one another. As a result, the structures function as supramolecular assemblies, with individual units retaining excited states closely associated with each. The emission spectra resemble those of the mononuclear unit of lowest excited state energy – namely the Ru(II) unit – and the independence of the emission spectrum on excitation wavelength is indicative of fast energy transfer from the other units (Ir and/or Rh). The synthetic strategy is thus appealing in the rational design of systems for the channelling of energy to a specific location, for example, as required for light-harvesting in solar energy conversion.

## Experimental

NMR spectra were recorded using a Varian Inova-500 spectrometer and referenced to residual protio solvent resonances.  $^1\text{H}$  spectra were assigned by means of  $^1\text{H}$ - $^1\text{H}$  COSY and NOESY spectra. Electron ionization mass spectra were recorded using a Micromass LCT spectrometer, while high resolution spectra were obtained using a Thermo Finnigan LTQ FT at 100000 resolution with external calibration.  $[\text{Ir}(\text{Fppy})_2(\text{bpy})]^+$  was prepared in two steps from FppyH,  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  and bpy using the standard procedure for such complexes.<sup>[28]</sup> The synthesis of the boronate-substituted complex  $[\text{Ir}(\text{ppy})_2\{\text{bpy}-\phi-\text{B}(\text{OH})_2\}]\text{PF}_6$  has been reported previously;<sup>[15a]</sup> the analogous Fppy complex,  $[\text{Ir}(\text{Fppy})_2\{\text{bpy}-\phi-\text{B}(\text{OH})_2\}]\text{PF}_6$ , was prepared similarly, as described in the Supporting Information. The binuclear (IrRu) complexes **1** and **2** were prepared as described in our previous work.<sup>[15a]</sup>

*The synthesis and characterisation of all new mononuclear complexes, the intermediate binuclear and tetranuclear complexes, together with the tetranuclear complex 6, are given in the Supporting Information.*

### Synthesis and characterization of octanuclear $\text{Ir}_7\text{Ru}_1$ complex **5**.

A Schlenk tube was charged with  $[\{(\text{ppy}-\text{Br})_2\text{Ir}(\text{bpy}-\phi-\text{ppy})\}_2\text{Ir}(\text{bpy}-\phi-\phi-\text{bpy})\text{Ru}(\text{bpy})_2](\text{PF}_6)_5$  **4** (35 mg, 9  $\mu\text{mol}$ ),  $[\text{Ir}(\text{F}_2\text{ppy})_2\{\text{bpy}-\phi-\text{B}(\text{OH})_2\}]\text{PF}_6$  (42 mg, 41  $\mu\text{mol}$ ),  $\text{Na}_2\text{CO}_3$  (12 mg in 100  $\mu\text{L}$  water, 110  $\mu\text{mol}$ ) and DMSO (8 mL). The solution was thoroughly degassed via three freeze-pump-thaw cycles before adding  $\text{Pd}(\text{PPh}_3)_4$  (3 mg, 2  $\mu\text{mol}$ ) under a positive pressure of nitrogen. The solution was stirred at 80 – 85°C for 22 h. After this time, the DMSO solution was diluted with acetonitrile (5 mL) and filtered into saturated aqueous solution of  $\text{KPF}_6$ . The precipitate was collected using a centrifuge. Purification was achieved via column chromatography (silica gel) using gradient elution from 100% acetonitrile to 80% acetonitrile, 19.5% water and 0.5%  $\text{KNO}_3$ . After evaporation of solvent, the desired product was separated

from excess KNO<sub>3</sub> by selective dissolution into hot acetonitrile containing a drop of water. This solution was concentrated and filtered into saturated aqueous KPF<sub>6</sub> to precipitate the product as the PF<sub>6</sub> salt, which was collected using the centrifuge and washed with water (28 mg, 3.8 μmol, 42%). TLC (SiO<sub>2</sub>, 2% KNO<sub>3</sub> (aq), 18% H<sub>2</sub>O, 80% CH<sub>3</sub>CN): R<sub>f</sub> = 0.58. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN): δ 8.87 – 8.69 (m, 16H, H<sup>3</sup> and H<sup>3'</sup> on all bpy-φ units), 8.53 + 8.51 (2 d, 4H, bpy-H<sup>3</sup>), 8.38 – 8.28 (m, 14H), 8.25 – 8.17 (m, 14H, includes ppy-H<sup>3'</sup>), 8.14 (m, 63H, includes F<sub>2</sub>ppy-H<sup>4</sup> and ppy-H<sup>4</sup>), 7.87 – 7.65 (m, 28H, includes F<sub>2</sub>ppy-H<sup>6</sup> and ppy-H<sup>6</sup>), 7.60 – 7.54 (m, 7H), 7.46 – 7.32 (m, 11H, includes ppy-H<sup>5</sup>), 7.19 – 7.04 (m, 15H, includes F<sub>2</sub>ppy-H<sup>5</sup> and ppy-H<sup>5</sup>), 6.76 – 6.68 (m, 8H, F<sub>2</sub>ppy-H<sup>4'</sup>), 6.52 – 6.46 (m, 6H, ppy-H<sup>6'</sup>), 5.76 (d, 8H, *J* = 8.3, F<sub>2</sub>ppy-H<sup>6</sup>). <sup>19</sup>F NMR (200 MHz, CD<sub>3</sub>CN): δ –73.3 (d, *J*<sub>P-F</sub> = 750, PF<sub>6</sub>), –108.6 to –108.7 (m, F<sub>2</sub>ppy-F<sup>5'</sup>), –110.5 to –110.6 (m, F<sub>2</sub>ppy-F<sup>3'</sup>). MS (ES<sup>+</sup>): *m/z* = 672.4 [M – 9PF<sub>6</sub>]<sup>9+</sup>, 774.5 [M – 8PF<sub>6</sub>]<sup>8+</sup>, 905.6 [M – 7PF<sub>6</sub>]<sup>7+</sup>, 1080.9 [M – 6PF<sub>6</sub>]<sup>6+</sup>. HRMS (ES<sup>+</sup>): *m/z* = 672.3603 (measured), calcd for [C<sub>302</sub>H<sub>194</sub>N<sub>34</sub>F<sub>16</sub><sup>193</sup>Ir<sub>7</sub><sup>101</sup>Ru]<sup>9+</sup> = 672.3603; 774.4009 (measured), calcd for [C<sub>302</sub>H<sub>194</sub>N<sub>34</sub>F<sub>16</sub><sup>193</sup>Ir<sub>7</sub><sup>100</sup>Ru]<sup>8+</sup> = 774.4008; 905.4529 (measured), calcd for [C<sub>302</sub>H<sub>194</sub>N<sub>34</sub>F<sub>16</sub><sup>193</sup>Ir<sub>7</sub><sup>101</sup>Ru]<sup>7+</sup> = 672.4530.

**Synthesis and characterization of tetranuclear Rh<sub>2</sub>Ir<sub>1</sub>Ru<sub>1</sub> complex 9.** (Please see Supporting Information for legend to proton assignments in NMR).

A Schlenk tube was charged with [(ppy-Br)<sub>2</sub>Ir(bpy-φ-bpy)Ru(bpy)<sub>2</sub>][PF<sub>6</sub>]<sub>3</sub> **8** (18 mg, 0.0095 mmol), [Rh(pba)<sub>2</sub>{bpy-φ-B(OH)<sub>2</sub>}]PF<sub>6</sub> (21 mg, 0.024 mmol), Na<sub>2</sub>CO<sub>3</sub> (6 mg in 100 μL water, 0.057 mmol) and DMSO (8 mL). The solution was thoroughly degassed via 3 freeze-pump-thaw cycles before adding Pd(PPh<sub>3</sub>)<sub>4</sub> (2 mg, 0.0017 mmol) under a positive pressure of nitrogen. The solution was stirred at 80 - 85°C for 20 h. After this time, the DMSO solution was diluted with acetonitrile (4 mL) and filtered into saturated aqueous solution of KPF<sub>6</sub>. The precipitate was collected using a centrifuge (35 mg). Purification was achieved via column chromatography (silica gel) using gradient elution from 100% acetonitrile to 84% acetonitrile,

15.8% water and 0.2% KNO<sub>3</sub>. After evaporation of solvent, the desired product was separated from excess KNO<sub>3</sub> by selective dissolution into hot acetonitrile containing a drop of water. This solution was concentrated and filtered into saturated aqueous KPF<sub>6</sub> to precipitate the product as the PF<sub>6</sub> salt, which was collected using the centrifuge and washed with water (12 mg, 0.0035 mmol, 37%). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN): δ 9.74 (2 s, 4H, CHO), 8.87 – 8.69 (m, 8H, H<sup>D</sup>, H<sup>G</sup>, H<sup>d</sup>, H<sup>g</sup>, H<sup>d'</sup> and H<sup>g'</sup>), 8.53 and 8.51 (2 d, 4H, *J* = 7.8, bpy-H<sup>3</sup>), 8.33 and 8.31 (2 d, 2H, *J* = 7.4, H<sup>D'</sup>), 8.28 – 8.17 (m, 9H, ppyCHO-H<sup>3</sup>, H<sup>c</sup>, H<sup>C</sup> and H<sup>G'</sup>), 8.14 – 8.02 (m, 21H, bpy-H<sup>4</sup>, ppyCHO-H<sup>3'</sup>, ppyCHO-H<sup>4</sup>, H<sup>A</sup>, H<sup>a</sup>, H<sup>c'</sup>, H<sup>e</sup>, H<sup>h</sup> and H<sup>h'</sup>), 8.01 – 7.89 (m, 12H, H<sup>C'</sup>, H<sup>e</sup>, H<sup>H</sup>, H<sup>H'</sup>), 7.85 (dd, 1H, *J* = 5.9, 1.7, H<sup>f</sup>), 7.83 – 7.70 (m, 15H, ppyCHO-H<sup>6</sup>, bpy-H<sup>6</sup>, H<sup>A'</sup>, H<sup>a'</sup>, H<sup>e'</sup>, H<sup>f</sup> and H<sup>F</sup>), 7.65 and 7.64 (2 dd, 4H, *J* = 8.0, 1.6, ppyCHO-H<sup>4'</sup>), 7.58 (ddd, 1H, *J* = 7.4, 5.7, 1.0, H<sup>b</sup>), 7.53 (ddd, 2H, *J* = 7.6, 5.5, 0.9, H<sup>B</sup>), 7.46 – 7.39 (m, 5H, bpy-H<sup>5</sup> and H<sup>b'</sup>), 7.37 and 7.35 (2 overlapping dd, 4H, H<sup>F'</sup>), 7.26 and 7.24 (2 overlapping td, 4H, ppyCHO-H<sup>1</sup>), 7.15 and 7.14 (2 overlapping td, 2H, H<sup>B'</sup>), 6.79 (s, 4H, ppyCHO-H<sup>6'</sup>), 6.50 and 6.48 (2 d, 2H, *J* = 7.5, H<sup>E</sup>). ES<sup>+</sup> MS: *m/z* = 539.2 [M – 5PF<sub>6</sub>]<sup>5+</sup>/5, 710.2 [M – 4PF<sub>6</sub>]<sup>4+</sup>/4, 995.3 [M – 3PF<sub>6</sub>]<sup>3+</sup>/3. HR ES<sup>+</sup> MS: *m/z* = 537.50193 measured, 537.50192 calculated for [C<sub>148</sub>H<sub>102</sub>O<sub>4</sub>N<sub>18</sub><sup>191</sup>Ir<sup>103</sup>Rh<sub>2</sub><sup>96</sup>Ru]<sup>5+</sup>/5. TLC (SiO<sub>2</sub>, 2% KNO<sub>3</sub> (aq), 18% H<sub>2</sub>O, 80% CH<sub>3</sub>CN): R<sub>f</sub> = 0.55.

### Photophysical measurements

UV-Visible absorption spectra were recorded using a Biotech Instruments XS spectrometer. Samples were contained in quartz cuvettes with a path length of 1 cm. All spectra were run against a reference of pure solvent contained within a matched cell. Extinction coefficients were determined by a dilution technique and graphical application of the Beer-Lambert law. Steady-state luminescence spectra were recorded using a Jobin-Yvon Fluoromax-2 spectrometer, equipped with a Hamamatsu R928 photomultiplier tube. Quartz fluorescence cuvettes of path length 1 cm were employed and the absorbance of each solution at the excitation wavelength was below 0.1 to avoid inner filter effects. Emission was detected at right angles to the

excitation source with appropriate filters used where required to remove second order peaks. All emission spectra were corrected after data acquisition for dark count and for the spectral response of the detector. Excitation spectra were automatically corrected for lamp output through use of a beam splitter, which directs 8% of the excitation light to a reference photodiode. Luminescence quantum yields were recorded using a dilution technique with respect to a standard of ruthenium(II) tris(2,2'-bipyridine) chloride in aqueous solution ( $\Phi = 0.028$ ).<sup>29</sup>

Excited state lifetime measurements were measured using a time-resolved fluorescence spectrometer. Samples were excited in 1 cm pathlength quartz fluorescence cuvettes by third harmonic radiation (355 nm, ~1-2 mJ per pulse, pulse length ~7 ns) from a Q-switched Nd:YAG laser (Spectra Physics GCE-150-10). Stray light at 1064 nm (fundamental) and 532 nm (second harmonic) was removed by the use of optical filters. Emission was detected at right angles to the excitation source with a photomultiplier tube (Hamaatsu R298) and recorded using a digital storage oscilloscope (Tetronix TDS-340), before transfer to a PC for analysis. The raw data was deconvoluted to account for detector response by reference to a separate sample of 1,4-bis(5-phenyloxazol-2-yl)benzene (POPOP) or rhodamine, and fitted to an exponential decay by minimisation of the sum of squared residuals.

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